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Removal of copper (II) ions from aqueous solutions onto chitosan/carbon nanotubes composite sorbent

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ABSTRACT

Carbon nanotubes (CNTs) have been considered as promising materials in various applications including water treatment. Manipulation of CNT's with polymer offers unique properties as a composite in treatment of wastewater and removal of heavy metal ions. In the present work, we have developed a chitosan (CS)/multiwall carbon nanotubes (MWCNTs) composite sorbent by mixing the naturally occurring biopolymer CS and functionalized MWCNTs in 1% acetic acid solution. The obtained composite adsorbent was used successfully for the removal of copper (II) ions from aqueous solutions. The influence of variable parameters like pH, concentration of the metal ion, amount of adsorbent, and contact time on the extent of adsorption was investigated by batch method. Graphical correlations of various adsorption isotherm models such as Langmuir and Freundlich have been carried out. The data were analyzed by the Lagergren pseudo-first-order and pseudo-second-order kinetic models. Further the adsorption performance of the CS/MWCNTs composite was compared with CS and cation exchange resin. The maximum monolayer capacity of CS/MWCNTs composite and CS was found to be 454.55 and 178.57 mg/g, respectively. The prepared adsorbents were characterized by Fourier transform infrared spectroscopy and scanning electron microscopy analysis.

Keywords: Chitosan; Multi wall carbon nanotubes; Biosorption; Copper; Kinetics; Langmuir adsorption

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1. Introduction

Heavy metals are introduced into the environment naturally in the earth's crust or by anthropogenic activities. The natural bio-geochemical cycles of metals have been greatly affected by human intervention. The increasing development of industrial activities like mining, refining ores, fertilizer industries, manufacturing of batteries, pesticides and by the releasing of heavy metals from soils into streams are the main contributors to the contamination of water supplies by heavy metals [1–5]. The major toxic metals are copper, iron, chromium, vanadium, cobalt, nickel, lead, mercury, zinc etc. All of these elements possess the ability to interact with organic compounds by forming complexes. These modify the biological molecules by forming ligands with elements such as oxygen and nitrogen rendering the molecule inactive and unable to in appropriately function. As a result, heavy metals are considered to be hazardous to humans, as well as other life forms.

Copper is a naturally occurring substance which is found in the environment as "native copper" or within minerals. It can be found in industrial waste primarily in the form of bivalent ions as a hydrolysis product, $CuCO_3$ (aq), and/or organic complexes [6]. Copper is utilized in industries, as well as agriculture and these waste discharges contribute to an increase in the levels of copper (II) ion in the environment. These industrial processes, however, are not the only source of copper in wastewater. Copper is often emitted into the environment naturally by the decaying process of vegetation and combustion of fossil fuels. Though copper is essential for healthy bodily functions, it can be dangerous in high concentration in the body and can be cause of some diseases such as Wilson's disease, liver failure, and mental retardation.

The removal of heavy metals from wastewater can be achieved by chemical precipitation, ion exchangers, chemical oxidation/reduction, reverse osmosis, electro dialysis, ultra filtration etc. However, these methods have their drawbacks, such as incomplete metal uptake, which requires excess energy to generate; they are quite expensive to initiate, as well as to maintain. They also generate toxic waste which can create further pollution [7–10]. Therefore, the problems associated with the heavy metal ion pollution encourage the search for new technologies to eradicate these toxic metal ions from wastewater.

Biosorption is considered as a potential instrument for the removal of metal ions from waste solution and an alternative to the conventional processes [11]. There are several advantages of biosorption over conventional treatment methods; these include low cost, high efficiency, minimization of chemical and/or biological sludge, no additional nutrient requirement, as well as regeneration of biosorbent and a possibility of metal recovery. Several types of biosorbents have been considered to remove copper (II) ion from wastewater. Aman Tehseen et al. used potato peels charcoal as an adsorbent to remove copper (II) ions from aqueous solution [12]. Mohanty et al. used *Volvariella Volvacea* which is a fungus to remove copper from wastewater [13]. The cell wall of this fungus contains various biopolymer like chitin, amino acids, lipids, and polysaccharides. Zhan et al. focused on the effectiveness of the ferric salts in removing low levels of dosed copper from NOM-containing natural water [14].

CS appears to be a more economically and attractive sorbent for removal of metallic ions from water, since it is obtained from chitin the second most abundant polymer in nature next to cellulose. The presence of the amine and hydroxyl groups on the chitosan (CS) chain can act as chelation sites for metal ions and thus increasing its suitability as a biosorbent. CS is inexpensive and has many useful features: hydrophilicity, biocompatibility, biodegradability, and anti-bacterial property. Several methods have been used to enhance those properties and to facilitate mass transfer as well as to expose active binding sites present to further enhance the adsorption capacity. CS is effective in the uptake of transition metals since the amino groups on CS chains serve as coordination sites [15]. Several methods have been used to modify raw CS flakes either by physical [16–18] or chemical [19–21] modifications in order to improve pore size, mechanical strength, chemical stability, and biocompatibility.

The unique properties of carbon nanotubes (CNTs) such as its hollowness and layered tube structures, size distribution, high surface areas, electrical conductivity, semiconductivity and other various physical, chemical, and mechanical properties allow it's usage in several fields (photocatalysis, medicine, nanoscale electronics, hydrogen storage, mechanical systems etc.) [22–32]. Recently, the use of CNTs as reinforcing fillers into polymer matrices has gotten much attention. In order to achieve high performance and multi functions, CNTs in polymer/biopolymer matrix improve its mechanical and thermal strength, high electrical and thermal conductivity [33,34]. CNTs or inorganic fillers are generally embedded into polymer matrix through "melt blending" and "solution-casting" [35–39]. CS is one of the common polymers that used for the preparation of polymer/CNTs composites [40–43]. Several studies have investigated the use of CS/CNTs in various applications such as the adsorption [44], anodic stripping voltammetry [45], and biosensors [46].

In this study, we have developed CS/multiwall carbon nanotubes (MWCNs) composite sorbent for the removal of copper (II) ions from aqueous solutions. The adsorption capacity of the composite sorbent is compared with the CS beads and commercial cation exchange resin (CER). The effect of various parameters such as pH, initial metal ion concentration, adsorbent dosage, and contact time was studied by batch process. The biosorbents, before and after adsorption, were characterized by Fourier transform infrared spectroscopy (FTIR) spectral analysis and scanning electron microscopy (SEM) analysis to analyze the interaction between the metal and the biosorbent. The experimental data were fitted to Langmuir and Freundlich adsorption isotherm models, and the results were analyzed with pseudo-first-order and pseudo-second-order kinetic equations.

2. Materials and methods

2.1. Materials

CS, having an average molecular weight of 300,000, was purchased from Aldrich Chemical Corporation, USA. Multiwall CNTs (MWCNTs) (>98% carbon basis) with O.D. × L6–13 nm × 2.5–20 μm produced by chemical vapor deposition method were obtained from Sigma-Aldrich Company, USA. Analytical grade of copper sulfate and ammonium sulfate was purchased from Fisher Scientific Company for copper (II) ion source. Hydrochloric acid and sodium hydroxide used for pH adjustment and acetic acid for CS dissolution and other acids were obtained from Aldrich Chemical Company. CER was obtained from Taiwan. Distilled water was used in all of the experimental works.

The stock solutions of copper (II) were prepared by dissolving 3.929 g of hydrated copper sulfate in 1,000 mL of double-distilled water such that each milliliter of the solution contained 1 mg of divalent copper ion. The exact concentration of each metal ion solution was calculated on mass basis and expressed in terms of mg L^{-1}. The required lower concentrations were prepared by dilution of the stock solution. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

2.2. Preparation of biosorbents

2.2.1. Chitosan

CS solution was prepared by adding 3 g of CS in 100 mL of 1% acetic acid solution under continuous stirring at 55˚C for about 3 h to facilitate the formation of a gel. The viscous gel was allowed to stay overnight so that all gas bubbles can escape. The CS solution was then transferred slowly into a 500 mL of 0.1 M NaOH solution drop wise and allowed to stand for a further four hours to facilitate the formation of the beads. The beads were separated from the NaOH bath and washed several times with deionised water until a neutral pH was achieved. They were dried in an oven at 50˚C.

2.2.2. CS/MWCNTs composite sorbent

Raw MWCNT's surface was functionalized through acid washing process with 3:1 ratio (by volume of concentrated sulfuric acid (H_2SO_4) and nitric acid (HNO_3)). Thus, the acid washing MWCNTs can be dispersed in organic solvent easily. One gram of nanotubes was added to 100 ml of the acid mixture in round bottom flask and refluxed at 80°C for 4 h. The resultant mixture was cooled and washed with double-distilled water until achieving neutrality of water. The MWCNTs were separated from water by filtration and dried under the vacuum at 60°C for further use.

0.1 g of surface activated MWCNTs was placed in 1% acetic acid solution and was stirred at 1,100 rpm for thirty minutes. Then, 3 g of CS was slowly added to the solution under continuous stirring at 55˚C for about 3 h to facilitate the formation of viscous gel. The resultant CS/MWCNTs slurry was then transferred into beads by above-mentioned process. Five different beads of the completely dried sample were taken randomly, and the size of the each bead was measured by using the micrometer screw gauge with an accuracy of ± 0.01 mm. The average size of the bead was found to be 2.02 mm.

2.3. Equilibrium adsorption studies

A copper stock solution was diluted to required concentrations for analysis. Equilibrium batch adsorption experimental studies were carried out with a known weight of absorbent (0.1 g) and 100 mL of copper (II) ion solution of desired concentration at optimum pH (5.0) in 125 ml stopper bottles and were agitated at 150 rpm with a mechanical shaker. After attaining equilibrium, the adsorbent was separated by filtration and the aqueous-phase concentration of metal was analyzed using the UV–vis spectrophotometer (Genesys 10S, Thermo Scientific) illustrating the wavelength of maximum absorption of the copper ion to be 645 nm. Two drops of aqueous ammonia

(14.8 M) were added to the cuvette containing the copper ion solution in order to maximize absorbance before each reading. The effect of maximum adsorption time, pH, metal ion concentration, and adsorbent dosage on extent of adsorption was studied. The equilibrium adsorption capacity for each sample was calculated according to mass balance equation;

$$q_e = \left[\frac{C_i - C_e}{m}\right] \times V \tag{1}$$

where C_i and C_e are initial and equilibrium concentration, respectively, m is the mass of the adsorbent dosage in grams and V is the volume of the copper ion solution used in liters. Experiments were conducted with metal ion solution in the absence of adsorbent and it was found that there was no metal adsorption by the walls of the container.

2.4. Effect of pH

The effect of pH of the suspending medium on copper ion removal was studied by performing equilibrium sorption experiments at different pH values. Adjustments to the pH were made with 0.1 M hydrochloric acid and 0.1 M sodium hydroxide solutions. pH testing was carried out using Orion Dual Star Benchtop pH/ISE meter. The effect of pH was studied by keeping the metal concentration (100 mg/L), the amount of adsorbent (0.1 g), and temperature at a constant.

2.5. Characterization of biosorbents

The biosorbents CS and CS/MWCNTs were characterized using FTIR spectra, SEM micrograph, and surface area analysis. FTIR spectra of biosorbents were recorded before and after adsorption in a Shimadzu IR Affinity-1 spectrometer over the wave range 4,000–400 cm^{-1}. The samples were prepared as KBr disks. SEM photographs were taken with JSM 6700F Scanning Microscope to examine the morphology and surface structure of the beads at the required magnification at room temperature. The beads were deposited on a brass hold and sputtered with a thin coat of gold under vacuum. Acceleration voltage used was 20 kV with the secondary electron image as a detector.

2.6. Ion exchange capacity (IEC)

The IECs of the CS and CS/MWCNTs beads were estimated in order to get an idea of number of groups present before and after adding CNTs. Thus, IEC gives the number of milliequivalents of ions in 1 g of biopolymer beads. To determine IEC, specimens of identical weights were soaked in 50 mL of 0.01 N NaOH solutions for about 12 h at ambient temperature. The beads were then removed by filtration, and 10 mL of each filtrate was titrated against HCl (0.01 M) using phenolphthalein indicator. IEC was then calculated as:

$$\text{IEC} = \frac{(B - P)M_{\text{NaOH}}5}{m} \tag{2}$$

where B is the amount of HCl used to neutralize the blank sample and P is the amount of HCl used to neutralize the adsorbent beads. Here, 5 is the factor corresponding to the ratio of the amount of NaOH taken to dissolve the beads to the amount used for titration and m is the sample mass in grams.

3. Results and discussion

3.1. Characterization of biosorbents

The FTIR spectra of CS and CS/MWCNTs were shown in Fig. 1 in both pristine and metal loaded forms. The FTIR spectrum of CS and CS/MWCNTs before adsorption indicates the presence of predominant peaks at 3,451 cm^{-1} (–OH and –NH stretching), 2,897 and 2,901 cm^{-1} (–CH stretching), 1,653 cm^{-1} (–NH bending in –NH2), 1,389 cm^{-1} (–NH deformation vibration in –NH_2), and 1,085 cm^{-1} (–C–O–C– stretching). This reveals that all functional groups such as –NH_2, –OH, originally present in CS, were intact even after CNTs addition and were available for interaction with the metal ions. The FTIR spectra of sorbent after adsorption indicate a shift in absorption frequency of amino and hydroxyl groups. This may be attributed to the deformation of O–H and N–H bands as a result of interaction between the functional groups and metal ions [1]. The degree of adsorption of metal ions on CS is a distinguishable feature, which can be followed through Infrared Spectroscopy. Fig. 1(b) shows the FTIR spectrum of CS loaded with copper (II) ions. An interesting phenomenon was the sharp shift in the position and intensity of the bands after metal binding. From these observations, it can be concluded that –NH_2 and –OH are the binding sites for copper (II) ion adsorption on the biosorbents. According to Chui et al. [47], the amino groups of CS were the major effective binding sites for metal ions, forming stable complexes by coordination. Transport studies conducted by Findon et al. [48] suggested that copper is chelated with the NH_2 and OH groups in the CS

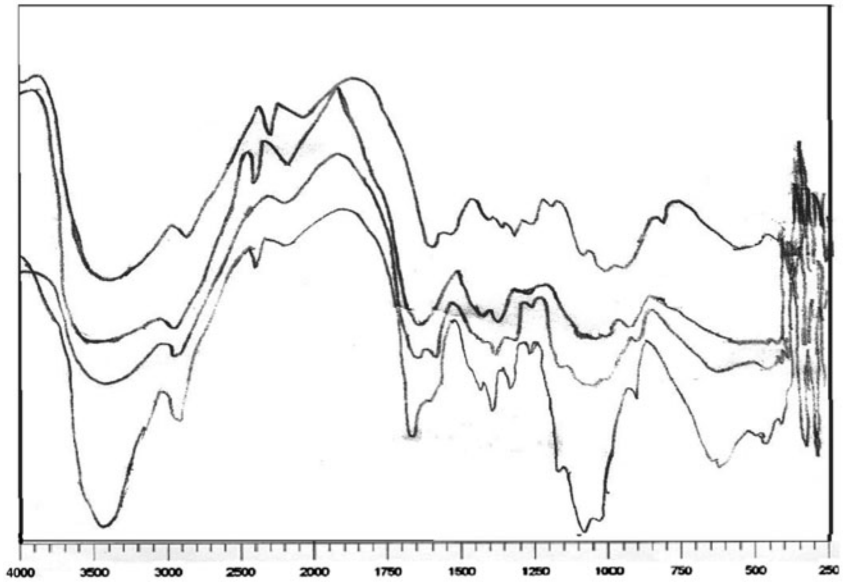

Fig. 1. FTIR spectra of (a) CS, (b) CS with copper, (c) CS/MWCNTs, (d) CS/MWCNTs loaded with copper.

chain. The nitrogen electrons present in the amino groups and some hydroxyl groups can establish dative bonds by donating electron pair with transitional metal ions. Therefore, deprotonated hydroxyl groups are involved in the coordination with metal ions [49]. It was established that CS forms chelates with metal ions by releasing hydrogen ions [50]. Formation of a complex between CS and copper (II) was shown in Fig. 2. Acid treated MWCNTs were capable of forming hydroxyl and carboxylic groups on their surfaces, results in the development of strong hydrogen-bonding with amino and hydroxyl groups of CS [51,52]. As the CNTs were functionalized with acid mixture through refluxing method, CS may have strong interaction with CNTs. This also improves the dispersion as well as the interfacial adhesion of CS and CNTs and dissolubility of MWCNTs in water. IEC values calculated from Eq. (2) also provided the evidence of additional functional groups after adding MWCNTs to the CS matrix. Residual ionic groups were generally estimated by IEC. The IEC values of Cs and CS/MWCNTs were 1.57 and 2.7 mequiv/g, respectively. Nearly half (41%) of the additional groups (hydroxyl and carboxylic) were available for copper (II) adsorption after dispersing CNTs into the CS matrix. Therefore, more adsorption of copper (II) ions was anticipated with CS/MWCNTs composite sorbent in the batch adsorption experiments.

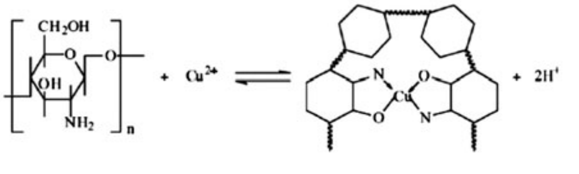

Fig. 2. Formation of complexation between CS and copper (II) ion.

SEM images of the biosorbents before and after copper ion sorption of CS and CS/MWCNTs were shown in Fig. 3. An examination of the SEM micrographs indicates the presence of multiple pores and additionally some cracks on the surface of the biosorbents. Usually, CNTs aggregate into bundles and entangle due to intrinsic Van der Waals attraction of the nanotubes. Fig. 3(c) and (d) shows that the MWCNTs were cylindrical in shape entangled together and form a clump. These images indicate that the MWCNTs were non-uniformly distributed within the CS matrix. Comparison of these micrographs before and after copper ion sorption indicates that there is no significant change in the morphology of the surface of the biosorbents.

3.2. *Effect of contact time and adsorption kinetics*

The effect of retention time on removal efficiency of copper (II) ions was studied by varying the contact time from 15 to 180 min, while keeping the concentration of metal ion (100 mg/L), absorbent dose (50 mg), and pH (5.0) constant. The effect of agitation time on the extent of adsorption of copper ion on CS and CS/MWCNTS was depicted in Fig. 4 indicating an increase in adsorption with time and attaining equilibrium at 90 and 120 min for CS and CS/MWCNTS,

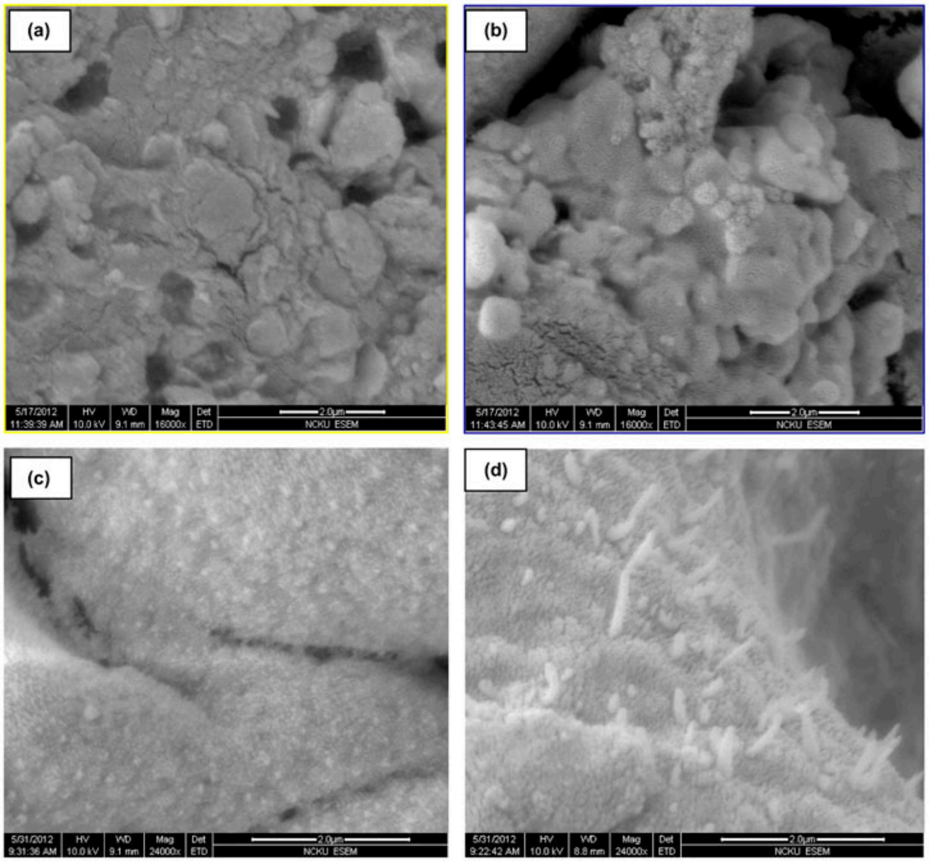

Fig. 3. SEM images of (a) CS, (b) CS loaded with copper, (c) CS/MWCNTs and (d) CS/MWCNTs loaded with copper.

respectively. After this equilibrium period, the amount of metal adsorbed did not change significantly with time. Although both CS and CS/MWCNTs reactions adsorption capacity of copper (II) ions increased with time, the adsorption rate was greater for CS/MWCNTs. This may be due to the presence of the functionalized MWCNTs that provide additional adsorption sites such as –COOH, –OH, or –C=O on the surface sites of CNTs for copper ion [53]. Additionally, embedding of functionalized CNTs into CS polymer matrix can form a homogeneous black dispersion in aqueous solution. There formation of electrostatic interaction between the positively charged polycation of CS and the negatively charged CNTs would decrease the van der Waals forces among CNT bundles by wrapping the CNTs in polymer chains. This would lead to the formation of interfacial gaps between gaps between polymer matrix and nanotubes that can adsorb metal ions [54,55].

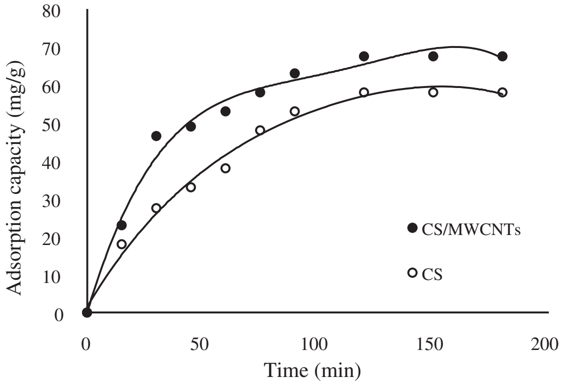

Fig. 4. Effect of time on biosorption of copper (II) ion on CS and CS/MWCNTs.

In the case of CER, the equilibrium adsorption was reached in 45 min with rapid ion exchange process. The concentration of copper (II) ion 100 mg/L at pH 4.0 and the amount of CER 100 mg were used in this experiment with 250 rpm agitation speed. Ion exchange resins were synthetic polymers that attached charged species which can exchange same charged species present in solutions. The CER used in this study was sulfuric acid cross-linked polystyrene beads with size 0.5–1 mm in diameter. CER exchange the ions according to the affinity of the individual species for the fixed negatively charged sites on the resin. The ion of interest in this study, copper (II) can easily replace the hydrogen ion initially in place on the sulfonic acid group. The time taken for equilibrium was controlled by the rate of reaction. This was dependent on the speed at which the total displacement of H^+ ions from CER by copper (II) ions occurs. Though the removal rate of CER was greater compared with biopolymer CS and CS/MWCNTs sorbents, but economical aspect commercial CERs were not be a good alternative for water treatment applications.

In order to investigate the mechanism of sorption, the sorption kinetics of copper ion on CS and CS/MWCNTs biosorbents were studied on the basis of pseudo-first-order [56] and a pseudo-second-order [57] kinetic models and were represented as:

$$\log(q_{\mathrm{e}} - q_{\mathrm{t}}) = \log q_{\mathrm{e}} - \frac{k_{\mathrm{ad}}}{2.303} t \tag{3}$$

$$\frac{t}{q_{\mathrm{t}}} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{1}{q_{\mathrm{e}}} t \tag{4}$$

A straight line of log ($q_{\mathrm{e}} - q_{\mathrm{t}}$) versus t suggests the applicability of this kinetic model. q_{e} and k_{ad} were determined from the intercept and slope of the plot, respectively. In many cases, the first order equation of pseudo-first-order does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption process [57]. The second-order kinetic model assumes that the rate limiting step may be chemical adsorption. In many cases, the adsorption data could be well correlated by second-order rate equation over the entire period of contact time. The results of this present study indicate that the adsorption of copper on CS and CS/MWCNTs follows second-order kinetics. It was found that the correlation coefficient r^2 values for this model were higher compared to the r^2 values as obtained in the first order kinetics as shown in Table 1.

Table 1
Pseudo-first-order and pseudo-second order rate constants of copper (II) ion (100 mg/L) on CS and CS/MWCNTS

Adsorbent	Pseudo-first order		Pseudo-second order	
	k_1	r^2	k_2	r^2
CS	0.027	0.944	0.0012	0.991
CS/MWCNTs	0.027	0.923	0.0002	0.978

3.3. Effect of pH on copper (II) adsorption

pH effects the solubility of metal ions, concentration of counter ions on the functional groups of the adsorbent, and the degree of ionization of the adsorbate during reaction. In this study, the effect of pH on adsorption capacity of copper (II) ion was investigated in the pH range 2.0–5.5. The experiments were carried out at 100 mg/L of initial metal concentration with 50 mg adsorbent mass for 90 min equilibrium time. At pH values higher than 5.5, copper (II) ions precipitated due to high concentration of OH^- ions. The data regarding the effect of pH on the extent of adsorption were given in Fig. 5. It was observed that an increase in pH from 2.0 to 5.0 resulted in an increase in the uptake of copper and maximum uptake occurred at pH 5.0 by both CS and CS/MWCNTs. The maximum equilibrium biosorption capacities obtained at this pH for CS and CS/MWCNTs were 48 and 88 mg/g, respectively. This shows that the CS/MWCNTs were adsorbing copper (II) ions at a faster rate at the different pH values.

The effect of pH on adsorption capacity may be discussed on the basis of the nature of the chemical interactions of copper (II) ions with the biosorbents. The hydroxyl and amino groups present on the biosorbents were responsible for the binding of copper (II) ions. Low pH would favor protonation of the amino sites, resulting in a reversal of charge, and would greatly diminish the metal chelating ability of CS. Thus, the heavy metal cations are completely released under extreme acidic conditions. At higher pH, the free amino groups attract the positively charged copper (II) ions. This results in an increase in adsorption. According to Low et al. [58], at low pH values the surface of adsorbent would be closely

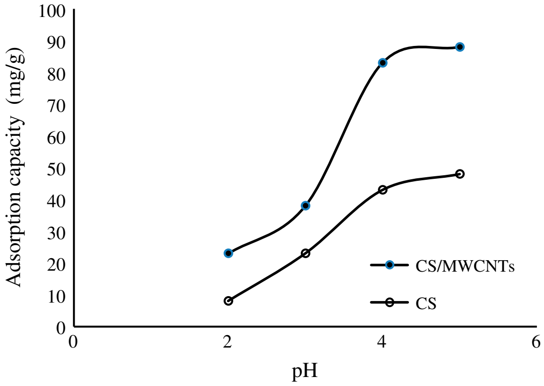

Fig. 5. Effect of pH on biosorption of copper (II) ion on CS and CS/MWCNT.

associated with hydronium ions (H_3O^+) that hinder the access of the metal ions to the surface functional groups. The surface complex formation theory also states that the competition of protons with metal ions on adsorption decreases with increase in pH value.

The effect of pH on exchange capacity of CER was tested within the range of pH 1.0–5.0 at room temperature, and maximum uptake of copper (II) ions was occurred at pH 4.0. CER have a capability of uptake metal ions over entire pH range; however, the decrease in metal ion uptake at lower pH was attributed to competition between hydrogen ions and copper ions. Strong acid cationic resins are highly dissociated and freely exchange ions at any pH. As pH decreases, the level of dissociation does, however, decrease making it more difficult for H^+ ions to be replaced by copper (II) ions. It can also be postulated that as the level of dissociation decreases the overall positive charge of the resin bead increases, leading to a repulsion of positively charged copper (II) ions [59]. This repulsion of copper ions would explain the decrease in adsorption capacity with pH, while the decrease in adsorption capacity as the pH increased from 4 to 5 can be linked to copper (II) having an increased affinity toward OH^- as pH increases.

3.4. Effect of adsorbent dose

Adsorbent dosage was an important variable controlling adsorption capacity in an adsorption process. The effect of CS and CS/MWCNTs dose on adsorption of copper ions was studied by varying the amount of adsorbent from 0.05 to 0.5 g while keeping the concentration metal ion solution (100 mg/L), time (90 min), volume of solution (100 mL), and pH (5.5) were constant. As the absorbent dosage increased, the % removal of copper (II) ions was increased from 11.5 to 61.5, and 16.5 to 71.5 with CS and CS/MWCNTs, respectively. This was expected because a fixed initial solute concentration increased adsorbent doses and provided greater surface area for adsorption sites. This may also be due to an increase in adsorption site per unit mass with increase in their particle size and because more opened sites are available to bind metals. The maximum % removal for CS and CS/MWCNTs was 61.5% and 71.5%, respectively. Fig. 5 shows the % removal of copper (II) ions adsorbed on CS and CS/MWCNTs at various amounts. It can be seen in Fig. 6 that CS/MWCNTs % removal was greater than that of CS as the absorbent dose was increased from 0.05 to 0.5 g.

CER exchange capacity dependence on adsorbent dosage was tested by preparing varying CER-copper ion mixtures with varying CER doses ranging from 200–800 mg. The removal percentage of copper (II) ion was reached to 94% with 200 mg of CER and slightly increased to thereafter reaching 96% with increasing CER dose from 200 to 800 mg.

3.5. Effect of initial metal ion concentration on copper (II) adsorption

The effect of initial metal ion concentration was studied by varying the concentration from 50 to 250 mg/L while keeping other parameters (contact time-90 min; adsorbent dose-50 mg; pH 5.5 and volume 100 mL) constant. The results obtained were illustrated in Fig. 7. From the figure, it was observed that an increase in metal ion concentration resulted an increase in the adsorption capacity for both CS and CS/MWCNTs. However, at 250 mg/L metal ion concentration, there was a decrease in adsorption capacity for the CS system. This could be attributed to saturation of the available coordinating sites; since, the adsorption capacity of CS/MWCNTs was continued with higher adsorption rate than the CS biosorbent.

With CER, the effect of the initial metal ion concentration was studied using varying concentrations from 400 to 1,100 mg/L. As illustrated in Fig. 8, the adsorption capacity increased steadily with equilibrium concentration. As expected, a decrease in the adsorbate concentration translated into a decreased incidence of ion exchange and therefore an increase in the final mass of copper (II) ions in solution.

3.6. Adsorption Isotherm

Analysis of equilibrium data was fundamental for the industrial application of biosorption since it gives information for comparison among different biomaterials under different operational conditions, designing,

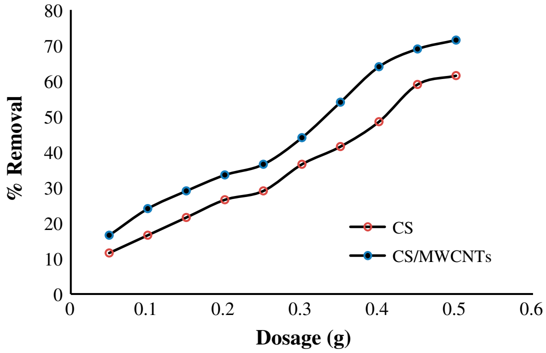

Fig. 6. Effect of adsorbent dose on percent removal of copper (II) ion using CS and CS/MWCNTs.

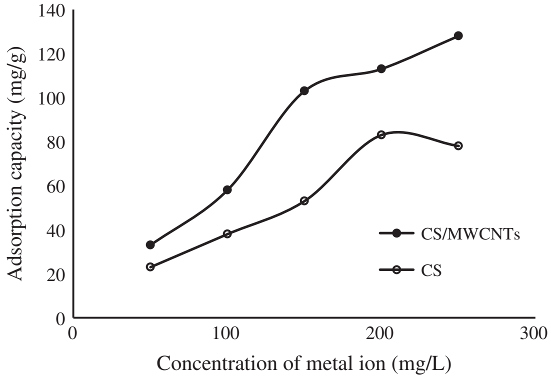

Fig. 7. Effect of initial metal ion concentration on adsorption of copper (II) ion.

and optimizing operating procedures [60]. To examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, sorption isotherm models were widely employed for fitting the data, of which the Langmuir and Freundlich equations were the most widely used. The isothermal studies were carried out in solution with concentration ranging from 50 to 250 mg/L while keeping pH (5.5), contact time (90 min), biomass (0.05 g) were constant.

Langmuir isotherm [61], used to describe the sorption phenomenon on homogenous surfaces and for a simple solute, was given by

$$Q_e = \frac{Q^0 b C_e}{1 + b C_e} \tag{5}$$

where C_e is the equilibrium concentration (mg/L), Q_e is the amount of copper (II) ion adsorbed for unit weight of CS or CS/MWCNTs, b is a constant related to the affinity of the binding sites and Q^0 represents a practical limiting biosorption capacity when the surface was embedded with copper ion.

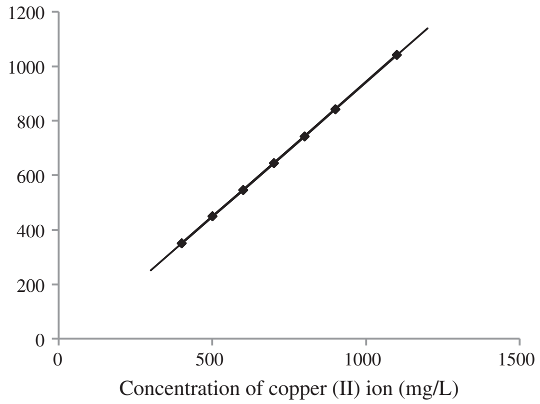

Fig. 8. Effect of copper (II) ion concentration on CER.

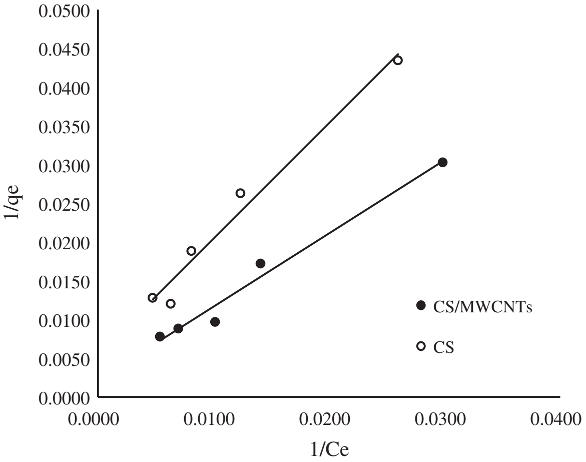

Fig. 9. Langmuir isotherm for copper (II) biosorption on CS and CS/MWCNT.

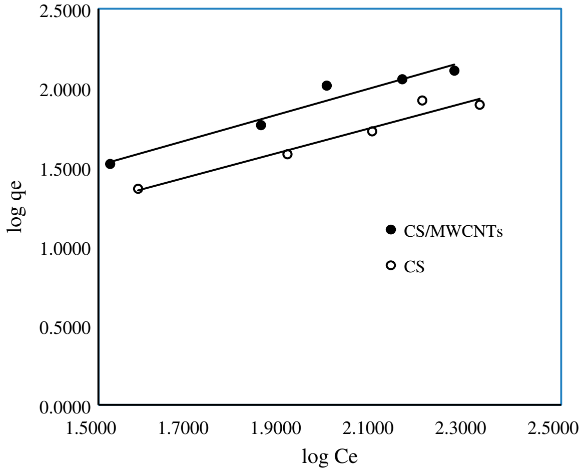

Fig. 10. Freundlich isotherm for copper (II) biosorption on CS and CS/MWCNT.

The linear form of the Freundlich isotherm [62] is represented by the equation,

$$Q_e = K_f C_e^{1/n} \tag{6}$$

K_f is a measure of adsorption capacity, and $1/n$ is the adsorption intensity. The parameters of Langmuir and Freundlich adsorption isotherms, evaluated from the linear plots (Figs. 9 and 10), were presented in Table 2 along with the correlation coefficients. The Q^0 of CS/MWCNTs appeared to be significantly higher than CS for copper (II) ion. Though both models represent the data adequately, according to the values of correlation coefficient, Langmuir isotherm well fitted the experimental data. However, the maximum

Table 2
Langmuir and Freundlich isotherm constants for adsorption of copper (II) on CA, and CS/MWCNTs

Biosorbent	Langmuir parameters			Freundlich parameters		
	Q^o (mg/g)	b (L/mg)	R^2	K_f	$1/n$	R^2
CS/MWCNTS	454.55	0.0023	0.9786	1.857	0.8281	0.9505
CS	178.57	0.0038	0.9758	1.284	0.7848	0.9527

adsorption capacity of CER was negative value of 131.58 mg/g and, thus, indicates the non-favor of adsorption. This is quite obvious as the mechanism work with CER was ion exchange.

4. Conclusions

In this study, CS/MWCNTs composite beads were successfully prepared and used as a biosorbing agent for the removal of copper (II) ions from an aqueous solution. The maximum uptake of copper ions occurred at pH 5.5. The sorption of copper (II) ions was heavily dependent on the amount of adsorbent, concentration of metal ion, contact time, and pH of the metal solution. The adsorption ability of CS/MWCNTs adsorbent for copper (II) ion was evaluated and compared its performance with CS plane beads. Furthermore, the biosorbent was characterized by ion exchange study, FTIR spectroscopy, and SEM techniques. The equilibrium adsorption data were correlated by Freundlich and Langmuir isotherm equations. The adsorption equilibrium data conformed well to the Langmuir model. The adsorption capacity of CS/MWCNTs was maximum and greater than CS. The maximum biosorption capacities of CS and CS/MWCNTs beads in this study were 178.57 and 454.55 mg/g for copper (II) ions, respectively. The kinetic studies indicated that the sorption of copper (II) ion on both CS and CS/MWCNTs followed a pseudo-second-order model.

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